Optical Materials 73 (2017) 89–94

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Temperature dependence of excitonic emission in $[(CH_3)_2NH_2]_3[BiI_6]$ organic–inorganic natural self assembled bimodal quantum dots

Haitham Abid [a,*], Amira Samet [a], Adnen Mlayah [b], Habib Boughzala [c], Younes Abid [a]

[a] Laboratoire de Physique Appliquée, Faculté des Sciences, Université de Sfax, Tunisia
[b] Centre d'Elaboration de Matériaux et d'Etudes Structurales (CEMES), CNRS-Université de Toulouse, 29 rue Jeanne Marvig, 31055 Toulouse, France
[c] Laboratoire des Matériaux et de Cristallochimie, Institut Préparatoire des Études Ingénieurs de Nabeul, 800, Mrezga, Nabeul, Tunisia

ARTICLE INFO

Article history:
Received 23 April 2017
Received in revised form
12 July 2017
Accepted 31 July 2017

Keywords:
Photoluminescence
Self assembled QDs
Temperature dependence
Modified Arrhenius equation
Exciton binding energy

ABSTRACT

This paper reports on the optical properties of organic – inorganic natural self assembled bimodal quantum dots (dimetylammonium) hexa-iodobismuthate $[(CH_3)_2NH_2]_3[BiI_6]$. The crystal structure consists of isolated BiI_6 octahedra, as inorganic ions, surrounded by dimethylamine cations. At room temperature, we investigate the optical properties by: UV/Vis absorption, ellipsometry, diffuse reflectance and photoluminescence. A broad Gaussian-shape luminescence band with a large stokes shift is observed in the red spectral range at 2.15 eV, due to radiative recombination of confined excitons in BiI quantum dots, suggesting that excitons are self trapped. The temperature-dependence of the PL emission is investigated. The observed S-shaped emission behavior is explained by thermal escape occurring at lower temperatures for high-energy dots and carriers being recaptured by dots emitting on the low-energy side of the distribution. A rate equation model, showing agreement with the experimental results, is used to investigate the thermal redistribution of the charge carriers. Exciton binding energies of 149.125 and 295.086 meV were determined from the modified Arrhenius analysis.

1. Introduction

The optical properties of semiconductor quantum dots QDs have been extensively investigated over the past decade and still attract a growing interest from both fundamental and applied points of view. These low dimensional systems bridge the gap between single molecules and bulk solid state, providing an opportunity to trace the evolution of electronic and optical properties of the matter from small atomic clusters to bulk solids. Because of quantum confinement, QDs possess size-dependent discrete exciton energy levels [1–8]. This feature allows for tuning of the spectral position of the absorption and emission bands of QDs by varying their size and makes them promising for tunable absorbers and emitters in applications such as light emitting devices [9–13] and biomedical fluorescent labeling [14–19]. However, the inhomogeneous size of dots constitutes the most dramatic problem that prevents the production of optoelectronic devices with a high quality of dots since it is incompetent to provide the prospect of temperature-independent low-threshold lasers [20,21]. In this case, growth conditions are primordially needed to improve the morphological details of QD-based semiconductor structures. In work to date, artificial methods such as molecular beam epitaxy and metal-organic chemical vapor deposition have been employed for obtaining low-dimensional materials [22,23]. On the contrary, chemical synthesis, which exploits self-assembly processes, also offers interesting opportunities for materials synthesis. The self-organization of molecules into highly ordered architectures with quantum dots structures has attracted a wide range of scientific and practical interest. Organic-inorganic iodo-bismuthates hybrids with the general formula (RNH_3) BiI, have the quantum dots structure by nature. In most cases, the inorganic frameworks are discrete clusters ranging from $[BiI_6]^{3-}$ [24] to $[Bi_8I_{30}]^{6-}$ [25]. The inorganic part, with a single atom scale thickness, serves as a quantum dot that has a very large quantum size confinement for electrons and holes. The organic barriers, which have a remarkably smaller dielectric constant, provide a great dielectric confinement effect on excitons in the inorganic dots. It is reported that both effects of these confinements on excitons lead to a very large binding energy of hundreds meV. This strong localization gives rise to a discrete, atomic-like, density of states. The discrete energy structure means that carriers trapped in dots are more likely to

---

[*] Corresponding author.
E-mail address: haithamlpa@yahoo.fr (H. Abid).

http://dx.doi.org/10.1016/j.optmat.2017.07.050

recombine radiatively, than though competing relaxation channels, such as defects or dislocations [26,27]. It is noteworthy that organic-inorganic hybrids representing an excitingly new class of solar absorber materials, have revolutionized the photovoltaic landscape because they have demonstrated a rapid and continuous increase in power conversion efficiencies rise up from 3.8% in 2009 to 21% in 2016 [28–37].

In the present work, we investigate the optical properties of tri (dimetylammonium) hexa-iodo-bismuthate $[(CH_3)_2NH_2]_3[BiI_6]$ as an organic - inorganic natural self assembled bimodal QDs compound [38,39]. A strong photoluminescence PL emission is observed in the red spectral range at room temperature. The temperature-dependence of the PL emission is investigated. The observed S-shaped emission behavior is explained by thermal escape occurring at lower temperatures for high-energy dots and carriers being recaptured by dots emitting on the low-energy side of the distribution. A rate equations model, showing agreement with the experimental results, is used to investigate the thermal redistribution of the charge carriers. This manuscript is organized as follows: we will describe in section 2 the experimental details and the measurement conditions; the experimental results are presented and discussed in section 3. The main findings of the work are summarized in the concluding section 4.

2. Experimental section

Preparation process and details on crystal structure determination can be found in Refs. [38,39]. The PL spectra were recorded using a Dilor XY triple spectrometer equipped with a CCD. The excitation wavelength was the 488 nm line of an argon laser. The sample temperature was controlled using a cold finger microcryostat. To avoid sample heating by the focused laser beam, we have limited the laser power density less than 0.1 $\mu W/\mu m^2$. PL measurements were possible with this very small power density due to the high emission efficiency of the sample. Moreover, a sufficiently long time between successive measurements was used to allow for thermalization of the sample. The optical absorption spectra of the spin coated films were deduced from direct transmission measurements performed using a conventional UV–visible spectrophotometer (HITACHI, U-3300). Diffuse reflectance spectra were recorded by focusing the light beam of a white lamp onto the sample and by collecting the elastically scattered light out of the specular directions. The light spot was imaged on the entrance slit of a 270 M Jobin-Yvon spectrometer. The sample consisted of packed microsized crystals adjusted between two glass slides. The reflected and transmitted beams in the specular directions were absent due to strong scattering. Ellipsometry measurements have been performed on pellets in the 1.55–4.68 eV (265–800 nm) optical range at Brewster incidence and using a UVISEL spectroscopic phase modulated ellipsometer [40]. To derive the complex dielectric function, we used a semi-infinite model [41], which allows one to establish a direct relation between the ellipsometric parameters (ψ, Δ) and the dielectric function. We are only interested to imaginary part which characterizes the absorption in our sample. We found a very good agreement over a wide spectral range.

3. Results and discussion

3.1. Crystal structure

Under ambient conditions, BiI_3 was dissolved in dimethylformamide (DMF) with excess HI. The mixture was stirred till it became clear and was stored at room temperature. Needle like orange crystals of $[(CH_3)_2NH_2]_3[BiI_6]$ were grown by slow evaporation. The X-ray diffraction measurements and detailed structural analysis of the title compound are given in our earlier publication [39].

In summary, $[(CH_3)_2NH_2]_3[BiI_6]$ crystallizes as an organic–inorganic hybrid material in the rhomboedric space group $R\overline{3}$, with a primitive unit cell of dimensions: a = 30.985 (8) Å, b = 30.985 (8) Å and c = 8.868 (4) Å. The crystal structure consists of isolated BiI_6 octahedra, as inorganic ions, surrounded by dimethylamine cations. Projection of the structure along the *c*-axe is given in Fig. 1. The asymmetric unit contains two crystallographic independent Bi atoms, Bi1 and Bi2. Each bismuth atom at the centre of the octahedron is connected to six iodine atoms at the corners. Bi1 ion has nearly ideal octahedral symmetry coordination while the Bi2 ion has a more distorted environment. Bi1–I distances range from 3.0919 (11) Å to 3.0921 (11) Å and I–Bi1–I bond angles vary from 87.73° (3) to 92.27° (3). Bi2–I bond lengths range from 3.0569 (11) Å to 3.108 (12) Å while I–Bi2–I ranges from 88.61° (4) to 91.40° (4). Hydrogen bonds are primary responsible for their observed arrangement of the components in the structure. In such a packing, the organic moieties form an insulator barrier separating the semiconductor isolated BiI_6 octahedra. This periodic structure can be regarded as an organic - inorganic self-organized bimodal quantum dot structure.

3.2. Optical properties

Fig. 2 shows the UV/Vis absorption, ellipsometry, diffuse reflectance and photoluminescence spectra of the title compound at room temperature. The UV/Vis absorption spectrum, showing a well agreement with the ellipsometric one, mainly consists of three bands at 2.62 eV, 3.04 eV and 3.52 eV corresponding to different optical transitions. At room temperature the spectrum is identical (intensity, shape and position) to that reported by G. C. Papavassiliou et al. [42] for the ($C_{32}H_{50}N_4OBiI_7$). This spectral identity is also clearly evident when observing the same orange color for the tow materials. It seems that the electronic properties (gap and mobility are roughly imposed by the inorganic parts while the cationic organic entities can influence the geometry of the inorganic framework).

By analogy, the band observed at 2.62 eV is due to a free exciton absorption which derives from the inorganic component of the structure. The band gap absorption is suggested to be at 3.04 eV, in good agreement with the orange color of the sample. The band with

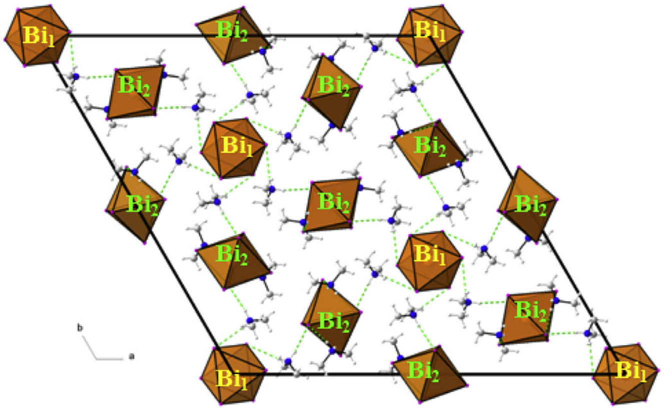

Fig. 1. Projection of the structure of $[(CH_3)_2NH_2]_3[BiI_6]$ along the *c*-axe. The asymmetric unit contains two crystallographic independent Bi atoms, Bi1 and Bi2. Each bismuth atom at the centre of the octahedron is connected to six iodine atoms at the corners. Bi1 ion has nearly ideal octahedral symmetry coordination while the Bi2 ion has a more distorted environment.